X-ray Fluorescence Holography at ALS

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INTRODUCTION

X-ray fluorescence holography (XFH) is a relatively new experimental tool for directly determining the local three-dimensional atomic structure around a given type of atom in an element-specific way [1-4]. This method is based on the same concept as photoelectron holography [5], but detects instead fluorescent x-ray photons. In the first type of XFH to be demonstrated experimentally [1], one measures the interference between the fluorescent radiation directly emitted by the excited atoms and additional wave components of the same radiation scattered by various near-neighbor atoms. One thus has to measure a given fluorescent intensity as a function of the direction of emission over as large a solid angle as possible. This method, for which the fluorescent atoms inside the sample act as sources and the intensity is measured in the far field, has been termed normal x-ray fluorescence holography (XFH) [2] or more specifically “direct XFH”. In parallel with the first direct XFH experiment, Gog et al. [2] proposed and demonstrated a different approach (termed multiple energy x-ray holography (MEXH) or “inverse XFH”) by applying the optical reciprocity principle and exchanging the roles of source and detector. In this case, the fluorescent atoms inside the sample become the detectors for the net field produced by the interference of the incident x-ray beam and the components of this beam that are scattered by near-neighbor atoms. MEXH is much faster, as the incident beam can be very intense, as emitted directly from a beamline monochromator, and one can furthermore in principle detect all of the fluorescence emitted above the sample surface. Here, one is thus measuring the total fluorescence yield of a given atomic transition as a function of the direction of the incident x-ray beam. Being able to measure at multiple energies also results in images with less aberration due to twin-image effects and other non-idealities [2,5]. Recent XFH/MEXH studies have demonstrated the ability to image a first-row element in the presence of a transition metal [3], and to study the local atomic environment in a quasicrystal, even though translational periodicity is lacking for such a system [4]. Current experiments are by and large detector-limited as to the speed of data acquisition.

We have thus initiated a program to develop x-ray fluorescence holography at the ALS. A new experimental system for carrying out MEXH experiments has been designed and assembled, and some first experimental results obtained with it are discussed.

EXPERIMENTAL SETUP

The experiment was performed on beamline 9.3.1, with the basic endstation configuration as shown in Fig. 1. Although originally designed to work at relatively low energies (<5 keV), the beamline has been reconfigured to work at higher energies (up to ~7 keV). Although some loss of flux from an ALS bending magnet is expected on going from 5 keV to 7 keV (approximately 35-40% for 1.9 Gev operation), and additional losses due to non-optimal use of various focussing mirrors was incurred, this energy extension was desirable for two reasons: (1) the resolution in MEXH is $\sim\lambda_x/2$, where λ_x is the incident x-ray wavelength, and thus to obtain adequate atomic resolution, the wavelength should be <2 Å; and (2) the incident photon energy has to be able excite a core electron of the atomic species under study, with 7 keV e.g reaching the K edges of most 1st-row transition metals. The fluorescence photons were collected by a 4-element Ge solid state detector designed by the LBNL Engineering Division and capable of up to 4 MHz count rate over its 4 cm^2 surface area. Fast single-channel analyzers were also used to discriminate the fluorescence photons from the elastically scattered photons and other fluorescent x-rays. We have also used fast interface and acquisition electronics to permit synchronizing rapid motor movements and data channel selections so as to suppress photon beam instabilities and time-dependent I_0 effects. Holograms are measured by rotating in a spiral-like motion, with the

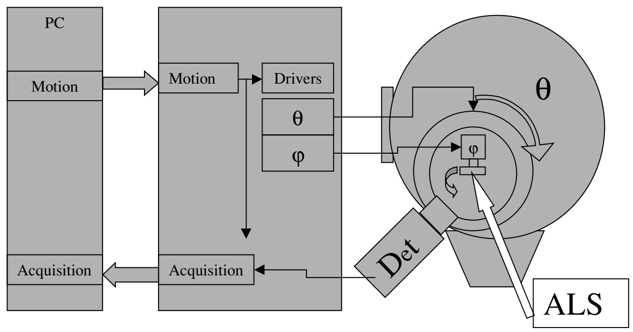

Figure 1. Experimental setup: At right is the sample chamber, with the Ge solid-state detector and automated sample rotations on the θ and φ axes shown. At left is the PC-based control and acquisition system, with synchronization of the motor movements and the data acquisition.

azimuth φ at 3600°/sec, and the elevation θ at 2^0/second. The measurement is performed over nearly the full hemisphere above the sample ($\theta<80^0$, with θ measured relative to the surface normal). The data sampling and acquisition is performed at every φ motor micro-step (with 800 μsteps per one 360° turn). A full hologram of 3×10^5 data points was thus recorded in less then one minute, and repeated several hundred times to yield a desired statistical accuracy.

RESULTS

As a first demonstration experiment we used a simple well-known single crystal, MnO with (001) orientation. The count rates varied between 1 and 4 MHz in initial tests at several energies, and thus the experiment was again detector, not beamline, limited. At the final setting of 6.93 keV, the count rates were up to 1 MHz, and safely in the linear region of the detector. In one data set, holographic scans of one minute were repeated about one thousand times, with a very conservative total of 10^{11} photons being collected in about 16 hours. For reference, to image the first neighbor Mn atoms with Z=25 electrons and at a distance $r \approx 3.1$ Å, the relative holographic signal is $\sim(Z\ r/r_e) \approx 2\times10^{-4}$, with r_e = the classical electron radius, and thus the minimum total number of photons to image these atoms is only about $10/(2\times10^{-4})^2 \approx 10^9$. Much more rapid data acquisition should thus be possible in the future. Additional non-statistical sources of noise in the ALS beam were removed by Fourier filtering.

The intensity variation of the Mn fluorescence as a function of the incident beam direction is shown in Fig 2(a). The lines, circles and ellipses are due to the long range periodicity of the crystal and represent x-ray standing wave (XSW) patterns or Kossel lines produced when the incoming beam satisfies the Bragg condition for some particular set of incidence directions. Fig. 2(b) shows a kinematical simulation of this XSW pattern using a program due to Len [6], with excellent agreement between experiment and simulation. Before proceeding with the holographic reconstruction, we used the symmetry information obtained from the XSW pattern to extend the hologram to the full solid angle. The holographic reconstruction was finally performed using the Helmholtz-Kirchoff integral transform (identical to a Fourier transform for data at a single energy), and this is shown in Fig 2(c) together with the known positions of the Mn atoms in the MnO crystal structure. The positions of about 25 near-neighbor Mn atoms are accurately determined to within about 0.2 Å. Due to the superposition of the real images and the twin, or dual, images typical of monochromatic holography, some of the atoms are suppressed [6]. In particular the nearest-neighbor Mn atoms are suppressed at the particular energy used. Further experimental data has been obtained at a different energy to help reduce such twin image effects, and these data are now being analyzed.

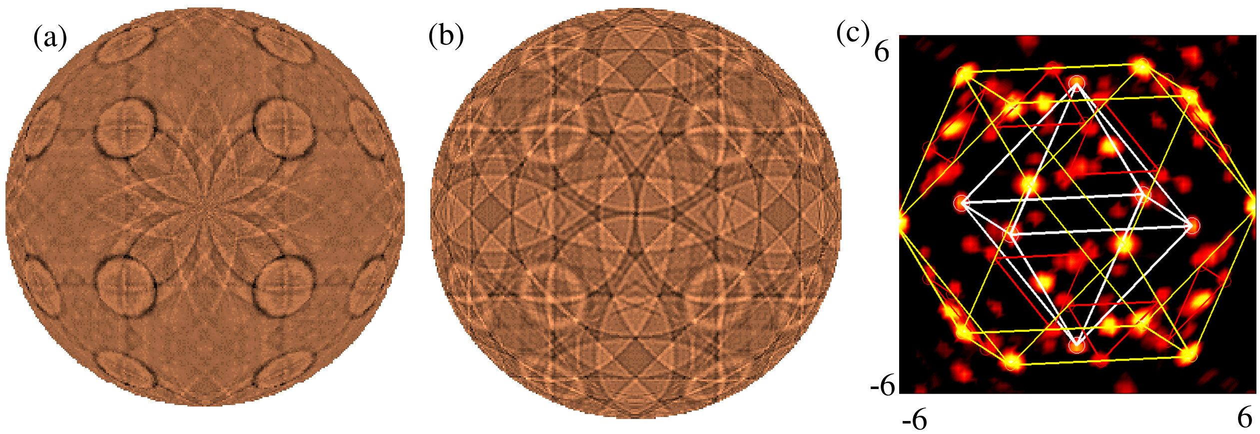

Figure 2. (a) The experimental x-ray fluorescence hologram of MnO, as excited by 6.93 keV photons and detected by Mn Kα photons at 5.9 keV. (b) As (a), but a kinematical theoretical simulation[6]. (c) Holographic image of Mn atoms in MnO as reconstructed via a Helmholtz-Kirchoff transform of the experimental data in (a). Scale units are Å.

CONCLUSIONS

We have carried out the first x-ray fluorescence holography experiments at the Advanced Light Source, with a bend magnet beamline providing sufficient fluxes to yield detector-limited, yet very reasonable, data acquisition times. The holographic reconstruction, together with the comparison of the experimental data with theoretical simulations, illustrates the high quality of the data that can be obtained. Future experiments will look at more complex materials.

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